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Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes

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ARL-TR-1879

March 1999

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Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes

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Abstract

We investigated the stability of aluminum at the high positive potentials encountered during the charging of lithium-ion cells. The electrolyte in these cells consists of solutions of lithium hexafluorophosphate and lithium methide in binary- and ternary-solvent mixtures of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. We performed the investigations with the controlled potential coulometry technique. We found that a protective surface film was formed on aluminum electrodes in these solutions and that this film protected the electrodes from further corrosion. The protective surface film was found to break down in lithium methide solutions at ~ 4.25 V versus a lithium reference electrode, and this resulted in increased corrosion of the aluminum electrodes at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in lithium hexafluorophosphate solutions was found to be quite stable and did not break down at potentials up to ~ 5 V.

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1. Introduction

The electrolytes used in commercial lithium-ion batteries freeze at approximately -30°C and thus their use is limited at lower temperatures. Recently, ethyl methyl carbonate (EMC) was identified [1] as a useful co-solvent for lithium-ion battery electrolytes. Since EMC freezes at -55°C , it can be used as a co-solvent to extend the liquidus range of the lithium-ion battery electrolytes. We investigated a number of electrolyte solutions in binary and ternary mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), and EMC and recently proposed [2] a 1.0-molar solution of lithium hexafluorophosphate (LiPF_6) in EC-DMC-EMC (1:1:1 vol %) as the electrolyte for low-temperature applications of lithium-ion cells. We found the new electrolyte to have good conductivity and electrochemical stability. We also found that Li/LiCoO_2 and graphite/ LiCoO_2 cells using the new electrolyte are operable at temperatures down to -40°C .

The corrosion of aluminum-alloy current collectors for the positive electrodes in lithium-ion batteries has created considerable concern. In a recent paper [3], we reported our results on the stability of aluminum in lithium imide (lithium tris-(trifluoromethane-sulfonyl) imide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) solutions. Aluminum was found to be unstable in these solutions at potentials above $\sim 3.5\text{ V}$ versus a lithium reference electrode. The instability of aluminum in these solutions at high positive potentials was attributed to the breakdown of the protective surface film on aluminum. We also found that the surface film could be modified by using lithium tetrafluoroborate additive to prevent the corrosion of aluminum in lithium imide solutions at the high positive potentials encountered during the charging of lithium-ion cells.

This report summarizes our investigation of the stability of aluminum in several low-temperature electrolytes based on solutions of LiPF_6 or lithium methide (lithium tris-(trifluoromethane-sulfonyl) methide, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$) in binary and ternary solvent mixtures of EC, DMC, and EMC.

2. Experimental Procedures

We used LiPF_6 (Hashimoto, Japan) and lithium methide (Covalent Associates) as received. Ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (all from Grant Chemicals) were dried over 4-Å molecular sieves before being used. Lithium foil (20-mil thick (Cypress-Foote Mineral Company)) packed over argon was opened in an argon-filled dry box (Vacuum Atmosphere Company) with a moisture content of less than 0.5 ppm.

We used a three-electrode system for all measurements. The reference and counter electrodes were both made by pressing lithium foil on a nickel screen. The working electrode consisted of a 1-mm-diam. aluminum wire that was heat-sealed in shrinkable Teflon[®] tubing. All potentials are referred to versus a lithium reference electrode.

We performed the controlled potential coulometry experiments with an EG&G Instruments, Inc., PAR (Princeton Applied Research), potentiostat/galvanostat (model 273). All experiments were computer-controlled using the EG&G PAR electrochemical analysis software (model 270). All experiments were performed inside a dry box.

3. Results and Discussion

We investigated the stability of aluminum in several LiPF_6 solutions in binary- and ternary-solvent mixtures of EC, DMC, and EMC. A number of these solutions had freezing points below $\sim -50^\circ\text{C}$ and thus were good candidates as electrolytes for low-temperature applications of lithium-ion cells. Table 1 shows the freezing points that we found for the various mixtures. The prefix numbers with each solvent mixture indicate the ratio of solvents by volume in each mixture, respectively. The aluminum electrode exhibited an initial potential of $\sim 1.8\text{ V}$ versus the lithium reference electrode in these solutions, but increased to $\sim 2.8\text{ V}$ and resulted in the formation of a surface film on the aluminum wire electrode. This film protects the aluminum substrates in lithium-ion batteries from further corrosion. The nature of the film on aluminum metal in these solutions has not been investigated but probably consists of aluminum fluoride or a species that contains fluoride.

Table 1. Freezing points of 1.0-mol/L solutions of LiPF_6 in various solvent mixtures.

Solvent mixture ratio (vol %)	Temperature ($^\circ\text{C}$)
1:3 EC-EMC	-65
1:4 EC-EMC	-75
1:1:1 EC-DC-EMC	-50
1:1:2 EC-DMC-EMC	-65
2:2:1 EC-EMC-DMC	-50
1:1:3 EC-DMC-EMC	-65

This study attempted to determine if the initial film formed on aluminum in these solutions was stable at the high positive potentials encountered during the charging of lithium-ion cells. We investigated the stability of aluminum at higher potentials by using the technique of controlled potential coulometry. The potential of the aluminum wire electrode dipped in the electrolyte was stepped up to a more positive value for 300 s, and the current response was plotted as a function of time. Typical plots obtained at potentials of 3.5 to 5.0 V in a 1.0-mol/L LiPF_6 solution in a binary 1:3 EC-EMC and a ternary 1:1:1 EC-DMC-EMC solvent mixture are presented in figures 1 and 2, respectively. Similar current density/time plots were obtained for aluminum electrodes in LiPF_6 solutions in other binary and ternary mixtures of EC, DMC, and EMC.

Figures 1 and 2 show that at each applied potential between 3.5 and 4.5 V, the current recorded at the aluminum electrodes quickly falls to a small steady-state value and shows no subsequent increase. Thus, the initial surface film formed on aluminum electrodes in LiPF_6 solutions appears to be quite stable and does not break down at potentials up to 4.5 V. At higher potentials, the current showed a slight increase after about 2 s. Since the LiPF_6 solutions in mixtures of EC, DMC, and EMC are known to undergo electrochemical oxidation [3] at potentials above $\sim 4.5\text{ V}$, the slight increase in current in the current density/time plots at 4.75 and 5.0 V may be regarded as due to the solvent oxidation. However, even at 4.75 V and 5.0 V, the steady-state currents were only slightly higher than

the steady-state currents at lower potentials. This indicates that the original protective film remains intact even at potentials above 4.5 V.

Recently, lithium methide solutions have been proposed [4–6] as thermally stable and highly conducting electrolytes for lithium-ion batteries. Therefore, we have also investigated the stability of aluminum in lithium methide solutions in several binary- and ternary-solvent mixtures of EC, DMC, and EMC. Typical current density/time plots obtained at aluminum electrodes at various potentials in 1.0-mol/L lithium methide solutions in a binary 1:3 EC-EMC and a ternary 1:1:1 EC-DMC-EMC solvent mixture are presented in figures 3 and 4, respectively. Similar plots were obtained in lithium methide solutions in other binary- and ternary-solvent mixtures of EC, DMC, and EMC.

The current density/time plots obtained at aluminum electrodes in lithium methide solutions were similar to those obtained in LiPF_6 solutions up to a potential of ~ 4.25 V only. At higher potentials, the current decreases initially but then begins to increase after ~ 100 ms. Also, the magnitude of the currents at potentials above ~ 4.25 V was much greater than that observed in LiPF_6 solutions. Therefore, it appears that the protective surface film initially formed on aluminum in lithium methide solutions breaks down at potentials above ~ 4.25 V. This results in high anodic currents due to the corrosion of the aluminum electrodes as well as the oxidation of solvents.

To compare the stability of aluminum in LiPF_6 and lithium methide solutions, we obtained the currents at various applied potentials from the current density/time presented in figures 1 through 4 at time $t = 200$ s and plotted in figure 5 as a function of the applied potential.

We see that the magnitude of the currents obtained at aluminum electrodes in LiPF_6 and lithium methide solutions is similar at potentials of up to ~ 4.25 V. At higher potentials, the currents in lithium methide solutions were much greater than those obtained in LiPF_6 solutions. Therefore, as shown before, it appears that in contrast to LiPF_6 solutions, the protective surface films formed on aluminum electrodes in lithium methide solutions are not stable at potentials above ~ 4.25 V.

Figure 1. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L LiPF_6 solution in 1:3 EC-EMC.

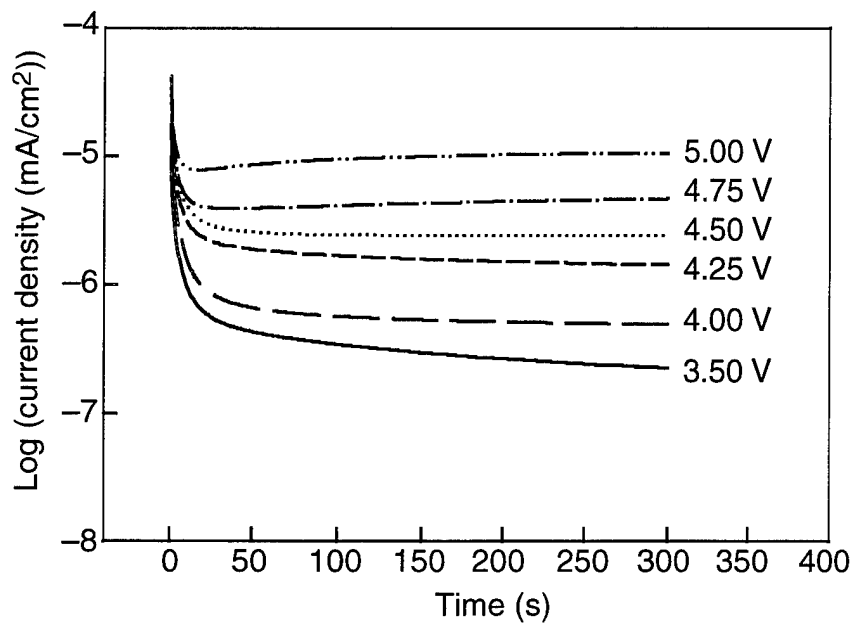


Figure 2. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L LiPF_6 solution in 1:1:1 EC-DMC-EMC.

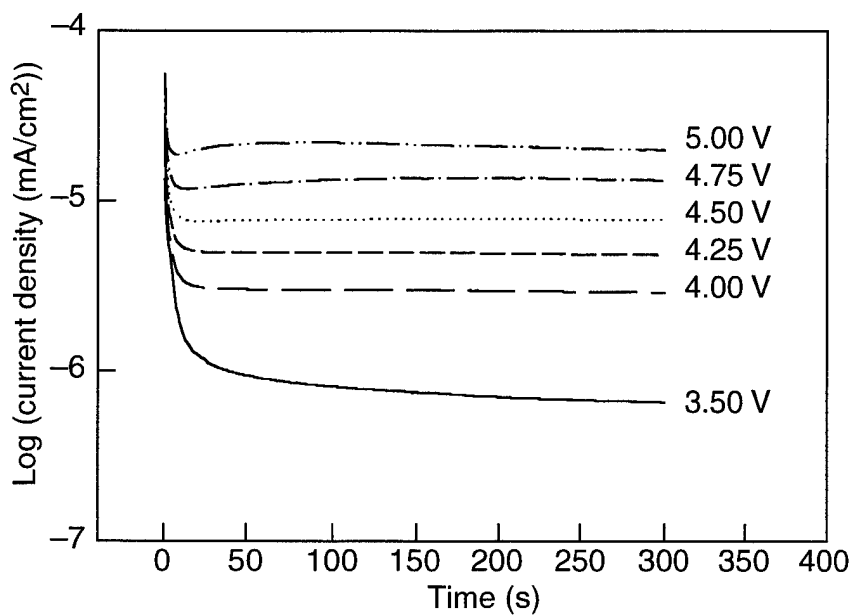


Figure 3. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:3 EC-EMC.

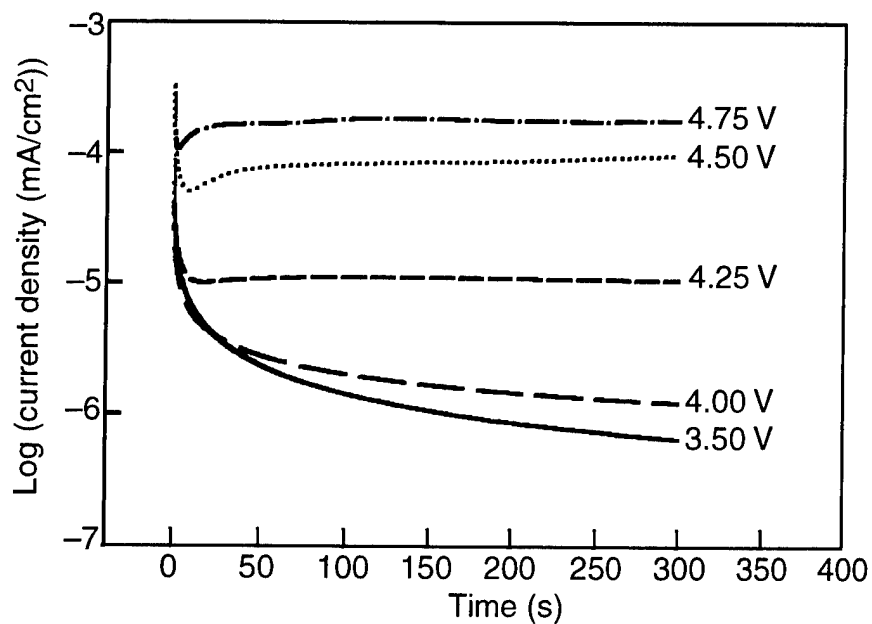


Figure 4. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:1:1 EC-DMC-EMC.

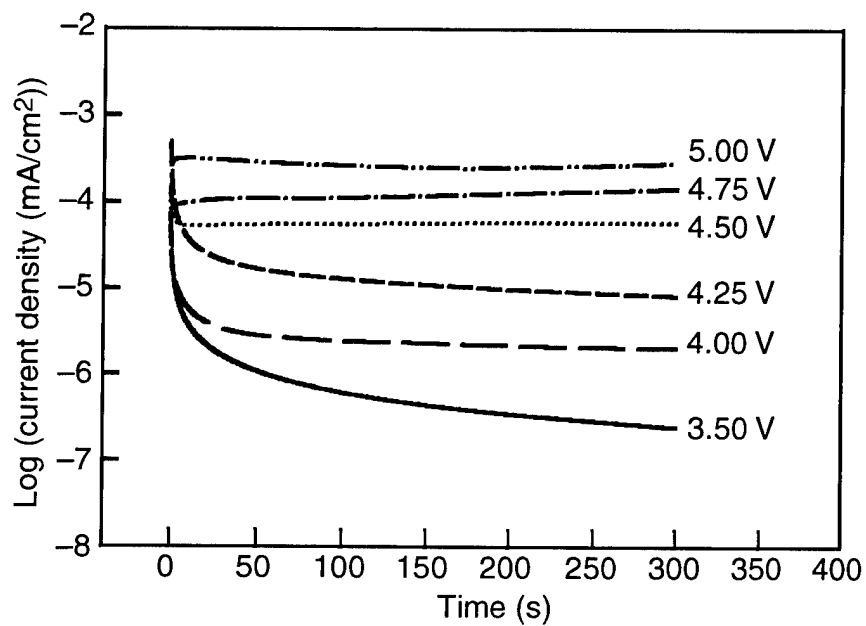
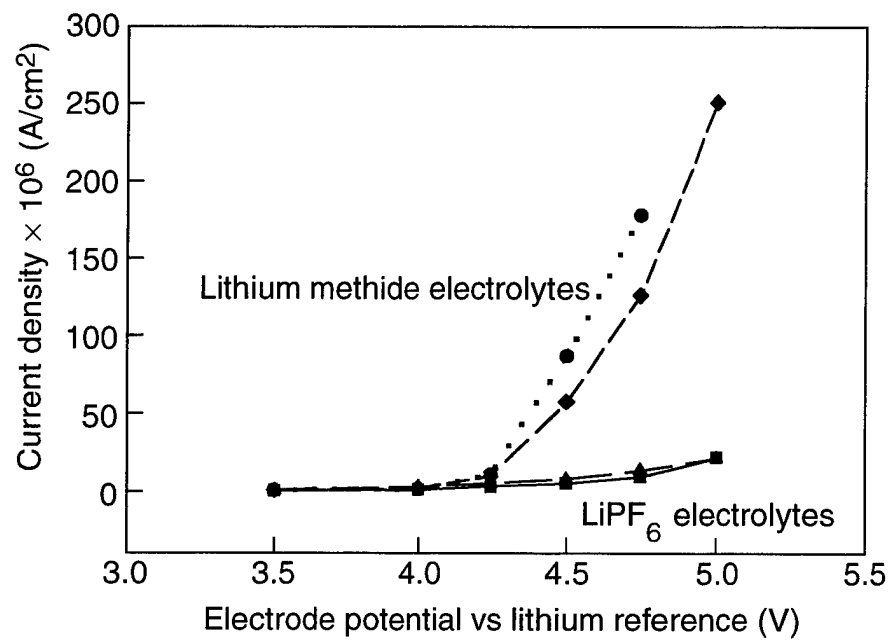


Figure 5. Current density vs applied potential plots at aluminum electrode in 1.0-mol LiPF_6 and lithium methide solutions in 1:3 EC-EMC (■,●) and 1:1:1 EC-DMC-EMC (▲,◆). Current densities were taken from current density/time plots presented in figures 1 through 4 at $t = 200$ s.



4. Conclusions

Controlled potential coulometric experiments showed that the protective surface film formed on aluminum electrodes in lithium methide solutions in binary- and ternary-solvent mixtures of EC, DMC, and EMC breaks down at potentials above ~ 4.25 V, and this results in increased corrosion at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in LiPF_6 solutions was found to be quite stable and did not break down at potentials up to ~ 5 V.

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 1999		3. REPORT TYPE AND DATES COVERED Progress, Oct 1997–Sept 1998
4. TITLE AND SUBTITLE Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes			5. FUNDING NUMBERS DA PR: AH94 PE: 62705A	
6. AUTHOR(S) Wishvender K. Behl (ARL), Edward J. Plichta (Communications-Electronics Command Research Development & Engineering Center)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Attn: AMSRL-SE-DC email: wbehl@arl.mil 2800 Powder Mill Road Adelphi, MD 20783-1197			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1879	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES ARL PR: 9NE6V1 AMS code: 622705.H94				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) We investigated the stability of aluminum at the high positive potentials encountered during the charging of lithium-ion cells. The electrolyte in these cells consists of solutions of lithium hexafluorophosphate and lithium methide in binary- and ternary-solvent mixtures of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. We performed the investigations with the controlled potential coulometry technique. We found that a protective surface film was formed on aluminum electrodes in these solutions and that this film protected the electrodes from further corrosion. The protective surface film was found to break down in lithium methide solutions at ~4.25 V versus a lithium reference electrode, and this resulted in increased corrosion of the aluminum electrodes at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in lithium hexafluorophosphate solutions was found to be quite stable and did not break down at potentials up to ~5 V.				
14. SUBJECT TERMS corrosion, methide hexafluorophosphate, ethylene carbonate, dimethyl, ethyl methyl			15. NUMBER OF PAGES 18	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	